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Accurate and Predictive Mixture Models Applied to Mixtures with CO_2

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Outline

Introduction and Motivation

Multi-Fluid Mixture Models

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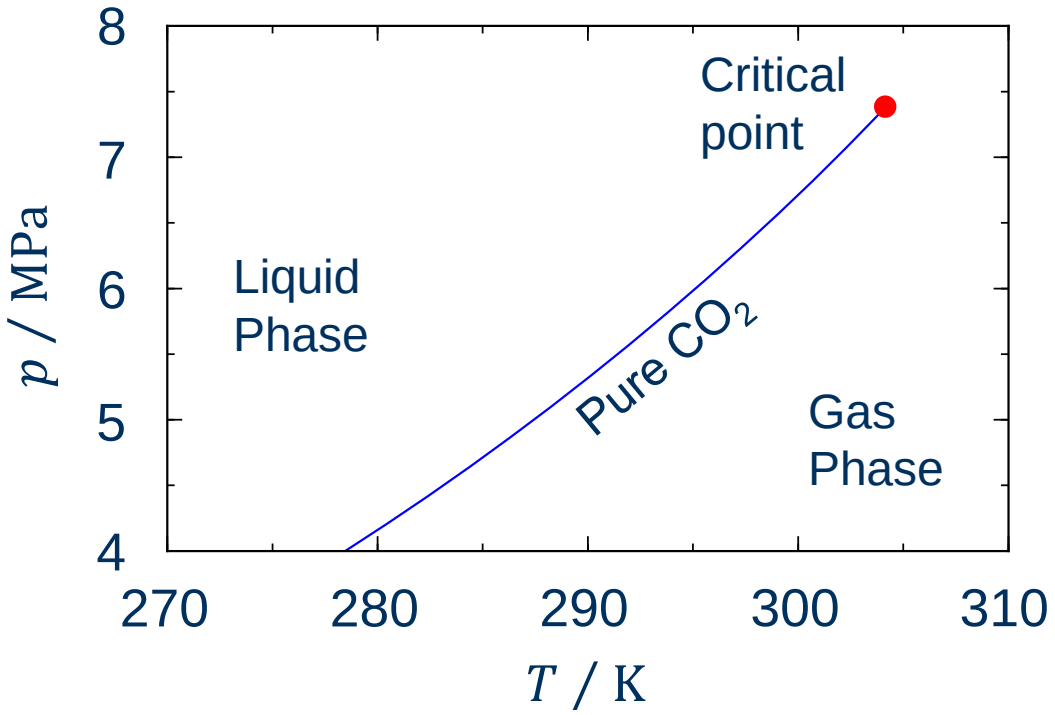
Results for Homogeneous Densities

Summary and Perspective

Introduction and Motivation

— The efficiency of processes with sCO_2 can be potentially optimized by using blends

— Example: Shift of critical point

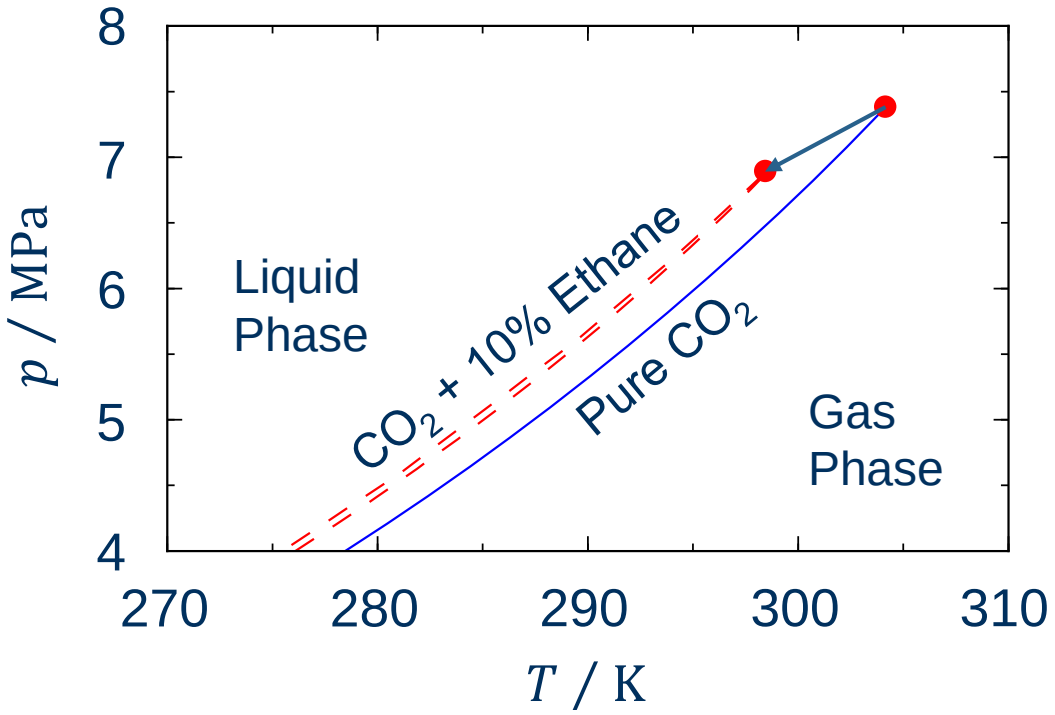


Introduction and Motivation

— The efficiency of processes with sCO_2 can be potentially optimized by using blends

— Example: Shift of critical point

Models needed to find promising mixtures



Introduction and Motivation

— Multiparameter equations of state (e.g. Span and Wagner (1996)) can be used in a multi-fluid mixture model (Lemmon and Tillner-Roth (1999), Kunz and Wagner (2012))

— For accurate models, usually many parameters need to be fitted to experimental data

— Standard mixing rules for predictive calculations do not always give good results

— Recently, we proposed a predictive model, which yields good results for phase equilibria

— Representation of homogeneous properties is studied in this work

— Here: CO_2+CH_4 and CO_2+C_2H_6 studied

Multi-Fluid Mixture Models

The multi-fluid mixture model can be written as follows

$$\frac{a}{RT} = \alpha(\tau, \delta, \bar{x}) = \sum_{i=1}^{N} x_i \underbrace{\alpha^{\mathrm{o}}_{\mathrm{o},i}(T,\rho)}_{\text{Pure substance}} + \underbrace{\sum_{i=1}^{N} x_i \ln(x_i)}_{\text{Ideal mixing}} +$$

Mixture of ideal gases:

No adjustable parameters

$$\sum_{i=1}^{N} x_i \underbrace{\alpha^{\mathrm{r}}_{\mathrm{o},i}(\tau,\delta)}_{\text{Pure substance}} + \underbrace{\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij} \alpha^{\mathrm{r}}_{ij}(\tau,\delta)}_{\text{Departure function}}$$

Residual part:

Arbitrary number of adjustable parameters

$$\alpha^{\mathrm{r}}_{ij} = \sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \alpha^{\mathrm{r}}_{ij,\mathrm{EXP}} + \cdots$$

Multi-Fluid Mixture Models

The multi-fluid mixture model can be written as follows

$$\frac{a}{RT} = \alpha(\tau, \delta, \bar{x}) = \sum_{i=1}^{N} x_i \underbrace{\alpha^{\mathrm{o}}_{\mathrm{o},i}(T,\rho)}_{\text{Pure substance}} + \underbrace{\sum_{i=1}^{N} x_i \ln(x_i)}_{\text{Ideal mixing}} +$$

$$\sum_{i=1}^{N} x_i \underbrace{\alpha^{\mathrm{r}}_{\mathrm{o},i}(\tau,\delta)}_{\text{Pure substance}} + \underbrace{\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij} \alpha^{\mathrm{r}}_{ij}(\tau,\delta)}_{\text{Departure function}}$$

$$\alpha^{\mathrm{r}}_{ij} = \sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \alpha^{\mathrm{r}}_{ij,\mathrm{EXP}} + \cdots$$

REF-MOD

Kunz and Wagner (2012)

Multi-Fluid Mixture Models

The reducing parameters are a function of the composition

$$\tau = \frac{T_{\mathrm{red}}(\bar{x})}{T} \qquad T_{\mathrm{red}} = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \beta_{T,ij}\gamma_{T,ij} \frac{(x_i + x_j)}{\beta_{T,ij}^2 x_i + x_j} \left(T_{\mathrm{c},i} T_{\mathrm{c},j}\right)^{0.5}$$

$$\delta = \frac{\rho}{\rho_{\mathrm{red}}(\bar{x})} \qquad \frac{1}{\rho_{\mathrm{red}}} = v_{\mathrm{red}} = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \beta_{v,ij}\gamma_{v,ij} \frac{(x_i + x_j)}{\beta_{v,ij}^2 x_i + x_j} \frac{1}{8}\left(\frac{1}{\rho_{\mathrm{c},i}^{1/3}} + \frac{1}{\rho_{\mathrm{c},j}^{1/3}}\right)^3$$

Multi-Fluid Mixture Models

If no experimental data are available

→ **Standard mixing rules** for reducing parameters

Linear mixing rules

$$\beta_T = 1 \;;\; \beta_v = 1 \;;\; \gamma_T = \frac{1}{2}\frac{\left(T_{c,i} + T_{c,j}\right)}{\left(T_{c,i} \cdot T_{c,j}\right)^{0,5}};\; \gamma_v = 4\frac{\left(v_{c,i} + v_{c,j}\right)}{\left(v_{c,i}^{1/3} + v_{c,j}^{1/3}\right)^3}$$

$$\rightarrow\; T_{red} = \sum_{i=1}^{N} x_i T_{c,i} \quad \text{and} \quad v_{red} = \sum_{i=1}^{N} x_i v_{c,i}$$

No departure function $\alpha_{ij}^{r} = 0$

LIN-MOD

Multi-Fluid Mixture Models

The multi-fluid mixture model can be written as follows

$$\frac{a}{RT} = \alpha(\tau, \delta, \bar{x}) = \sum_{i=1}^{N} x_i \underbrace{\alpha^{\mathrm{o}}_{\mathrm{o},i}(T, \rho)}_{\text{Pure substance}} + \underbrace{\sum_{i=1}^{N} x_i \ln(x_i)}_{\text{Ideal mixing}} +$$

$$\sum_{i=1}^{N} x_i \underbrace{\alpha^{\mathrm{r}}_{\mathrm{o},i}(\tau, \delta)}_{\text{Pure substance}} + \underbrace{\alpha^{\mathrm{DEP}}}_{\text{Departure function}}$$

Combination of Multi-Fluid Mixture Models with g^E-Models

The theoretically based departure function reads (Jäger et al. (2018a, 2018b))

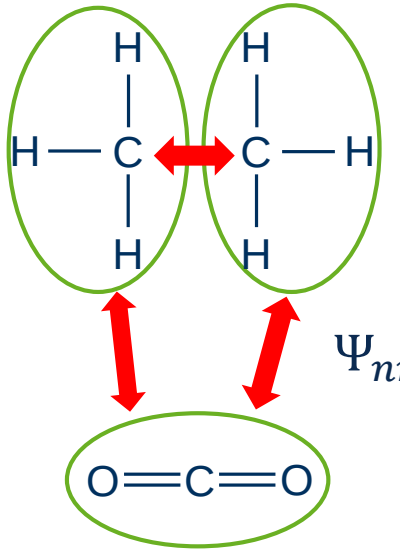
$$\alpha^{\mathrm{Dep}} = \frac{\ln(1+b\rho)}{\ln(1+b\rho_{\mathrm{ref}})}\left\{\frac{g_{\mathrm{GE}}^{\mathrm{E,r}}}{RT} - \sum_{i=1}^{N} x_i\left[\alpha_{\mathrm{oi}}^{\mathrm{r}}(\delta_{\mathrm{ref}},\tau) - \alpha_{\mathrm{oi}}^{\mathrm{r}}(\delta_{i,\mathrm{ref}},\tau_i)\right]\right\}$$

UNIFAC

Fredenslund et al. (1975)

Parameters of the VTPR (Schmid and Gmehling (2012), Schmid et al. (2014))

$$g^{\mathrm{E,r}} = RT\sum_{i=1}^{N} x_i \ln(\gamma_i^{\mathrm{r}})$$



$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right)$$

UNI-MOD

Combination of Multi-Fluid Mixture Models with g^E-Models

The theoretically based departure function reads (Jäger et al. (2018a, 2018b))

$$\alpha^{\mathrm{Dep}} = \frac{\ln(1+b\rho)}{\ln(1+b\rho_{\mathrm{ref}})}\left\{\frac{g^{\mathrm{E,r}}_{\mathrm{GE}}}{RT} - \sum_{i=1}^{N} x_i\left[\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta_{\mathrm{ref}},\tau) - \alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta_{i,\mathrm{ref}},\tau_i)\right]\right\}$$

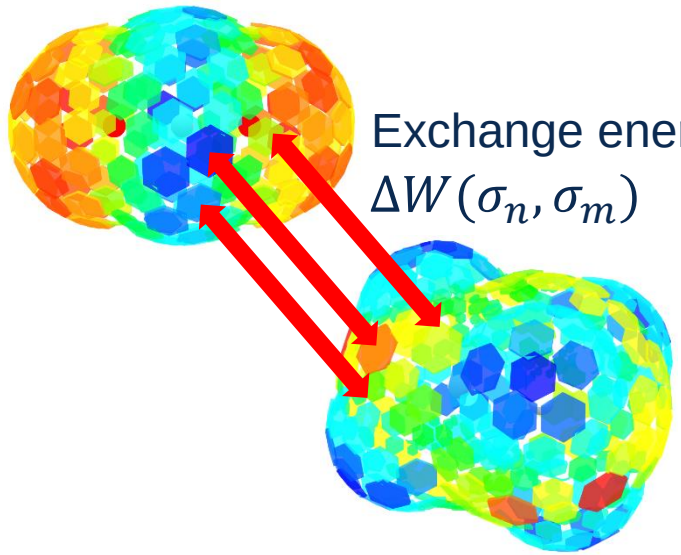
COSMO-SAC

Lin and Sandler (2002) (COSMO-SAC 1)

Hsieh et al. (2010) (COSMO-SAC 2)

Hsieh et al. (2014) (COSMO-SAC 3)

$$g^{\mathrm{E,r}} = RT\sum_{i=1}^{N} x_i \ln(\gamma_i^{\mathrm{r}})$$



COS1-MOD

COS2-MOD

COS3-MOD

Thermophysical Property Software (TREND)

— All models are implemented in a user-friedly software tool (TREND 4.0)

INPUT PARAMETERS

Path to EOS	D:\Arbeit\Stoffdatensoftwares\TREND_d	
Input code	tp	
Property 1	253	K
Property 2	1,85	MPa
Unit	molar	

Fluids	mole fractions	Eq. Type	Mix. Rules
co2	0,20	1	1
ethane	0,80	1	

FLASH CALCULATION

		vap	liq1	liq2	sol	hyd	Overall
temperature	K	253,000		253,000			253,000
pressure	MPa	1,850		1,850			1,850
density	mol/m³	1156,908		15243,80			4819,935
int. energy	j/mol	15520,343		6268,134807			7911,433
enthalpy	j/mol	17119,433		6389,496			8295,256
entropy	j/(mol K)	76,803		32,374			40,265
gibbs energy	j/mol	-2311,644		-1801,074			-1891,757
helmholtz energy	j/mol	-3910,735		-1922,435			-2275,580
isob. heat capacity	j/(mol K)	68,094		95,446			-6666,000
isoch. heat capacity	j/(mol K)	41,349		45,321			-6666,000
speed of sound	m/s	231,397		684,036			-6666,000
hydration number	-						
hydrate structure	-						
overall small cage occup	-						
overall large cage occup	-						
molecular weight	kg/mol	0,034		0,033			0,033
phase fraction	mol/mol	0,177611491		0,82238851			
x1	mol/mol	0,310125		0,176216			co2
x2	mol/mol	0,689875		0,823783706			ethane

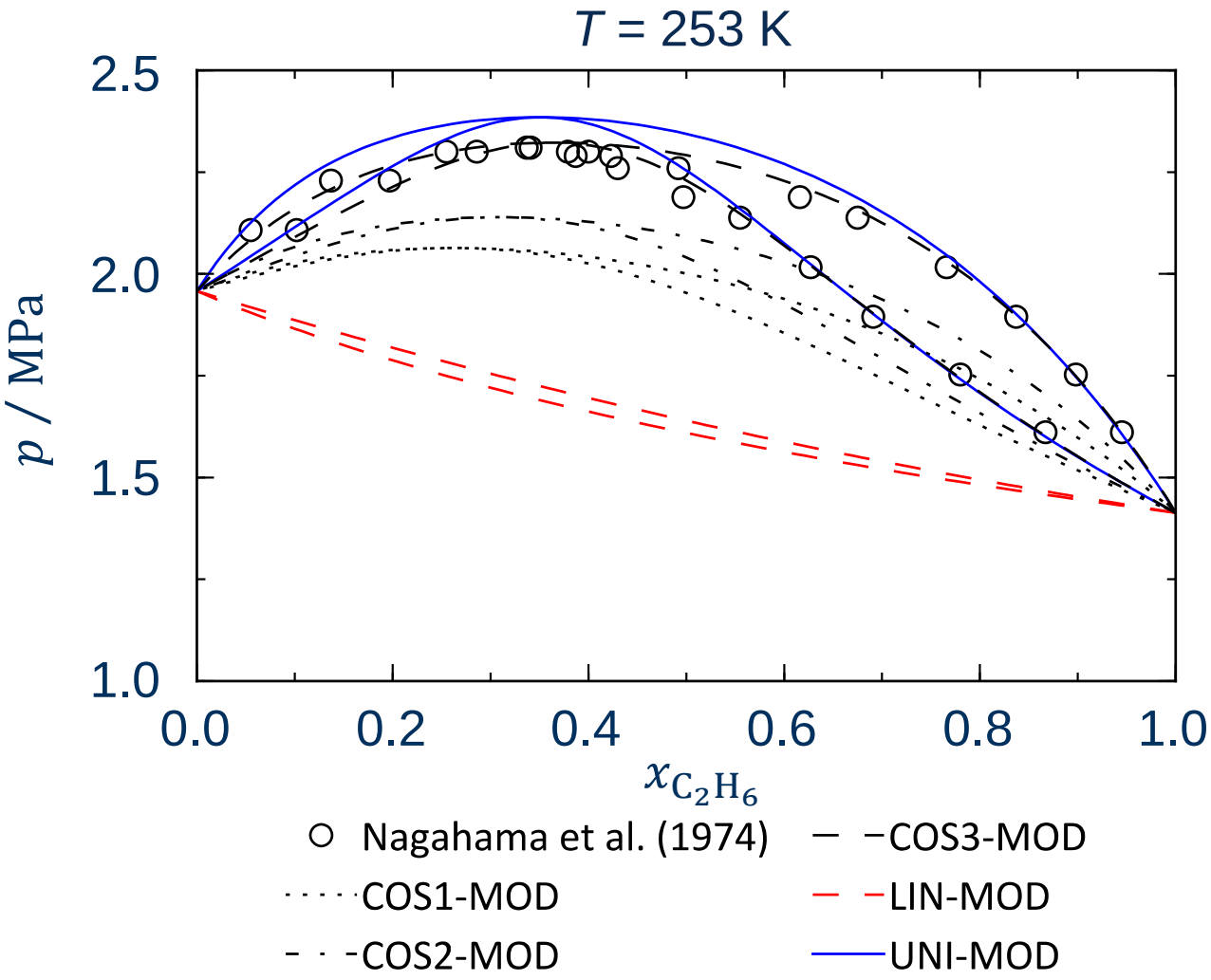
Results Phase Equilibria CO_2+C_2H_6

— Other models typically yield better results for phase equilibria than LIN-MOD

— COS3-MOD:

Adjusted dispersion parameter

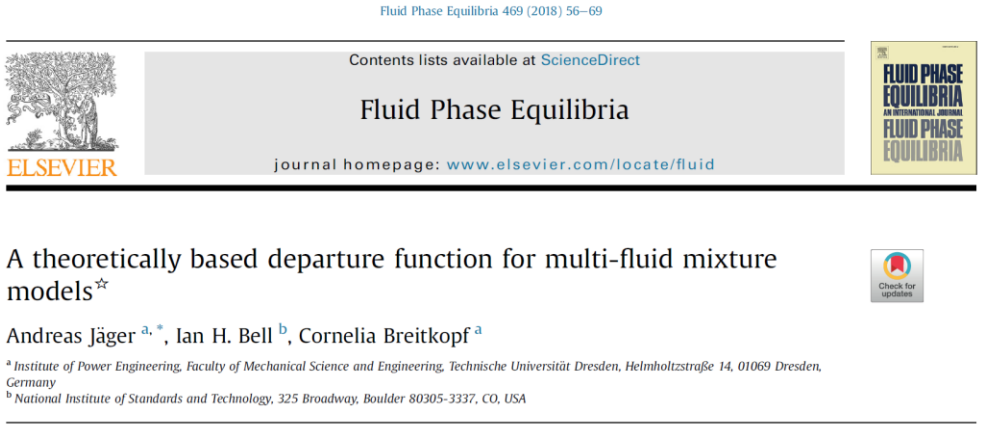
$$\frac{\varepsilon_{\mathrm{CO_2}}}{k_{\mathrm{B}}} = 85\ \mathrm{K}$$



Results Phase Equilibria CO_2+C_2H_6

— More results for phase equilibria can be found in our recent works

Jäger et al. (2018a)



Fluid Phase Equilibria 469 (2018) 56–69

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

A theoretically based departure function for multi-fluid mixture models☆

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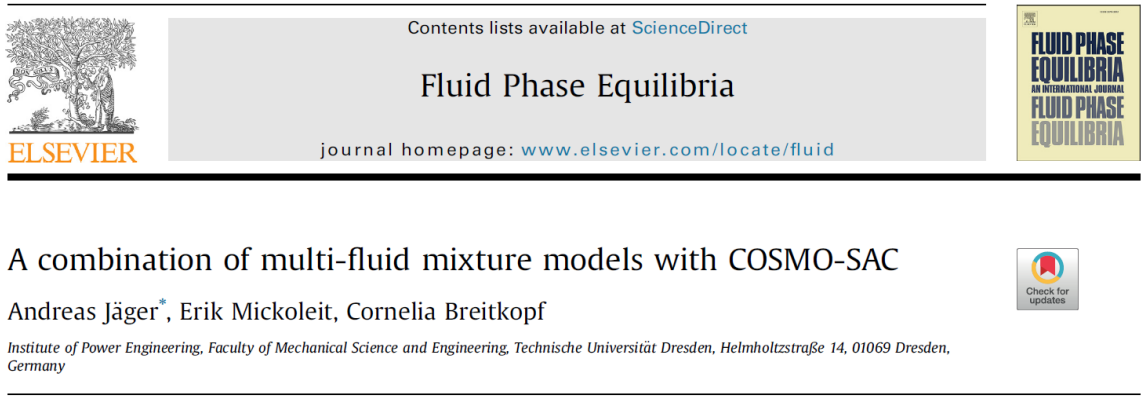
Jäger et al. (2018b)



Fluid Phase Equilibria 476 (2018) 147–156

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A combination of multi-fluid mixture models with COSMO-SAC

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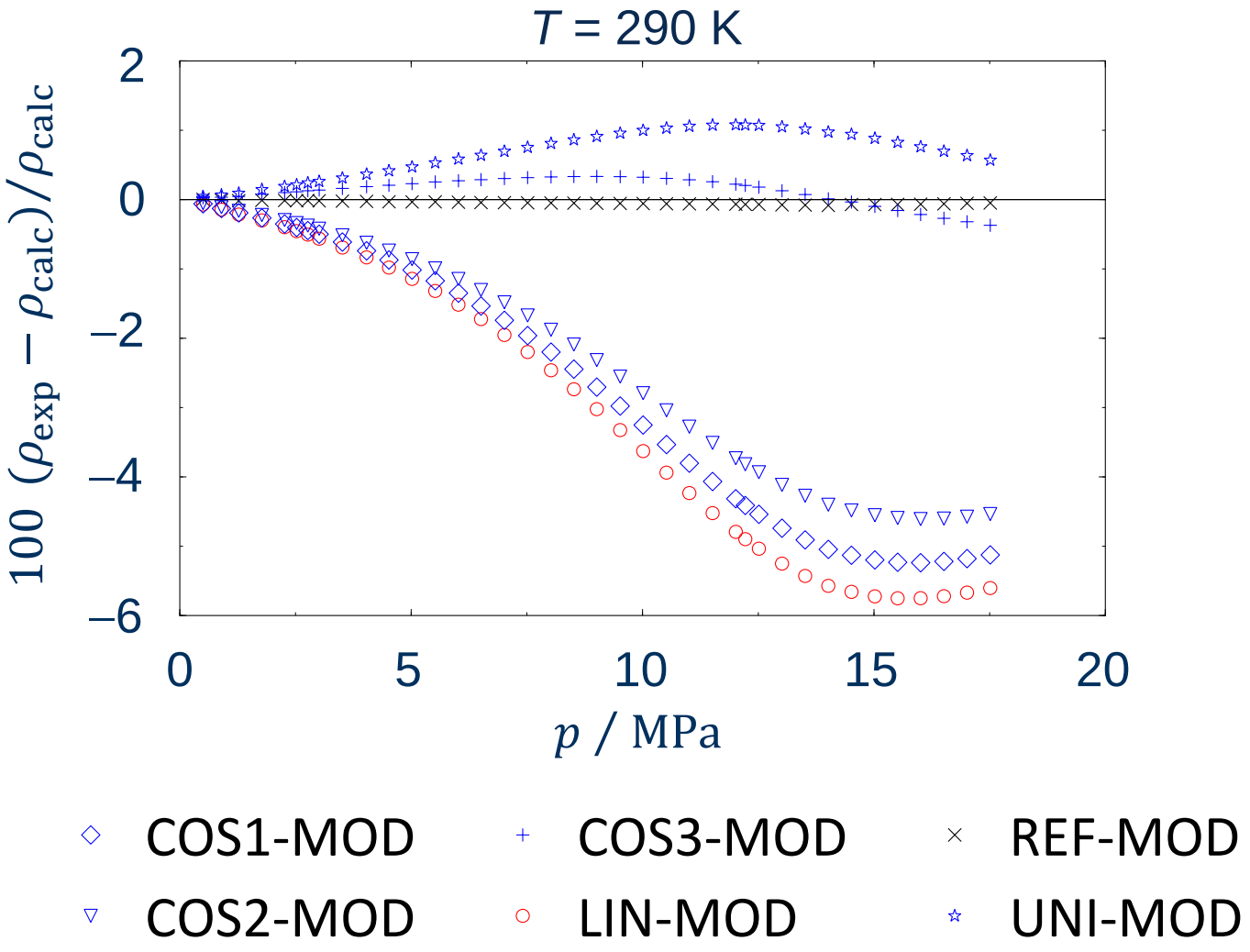
Results Homogeneos Densities CO_2+CH_4

- Experimental data by Jaeschke et al. (1991, 1997)
- Uncertainty of the data approx. 0.1%
- Tendency visible that predictive models UNI-MOD, COS1-MOD, COS2-MOD, COS3-MOD yield better results than LIN-MOD



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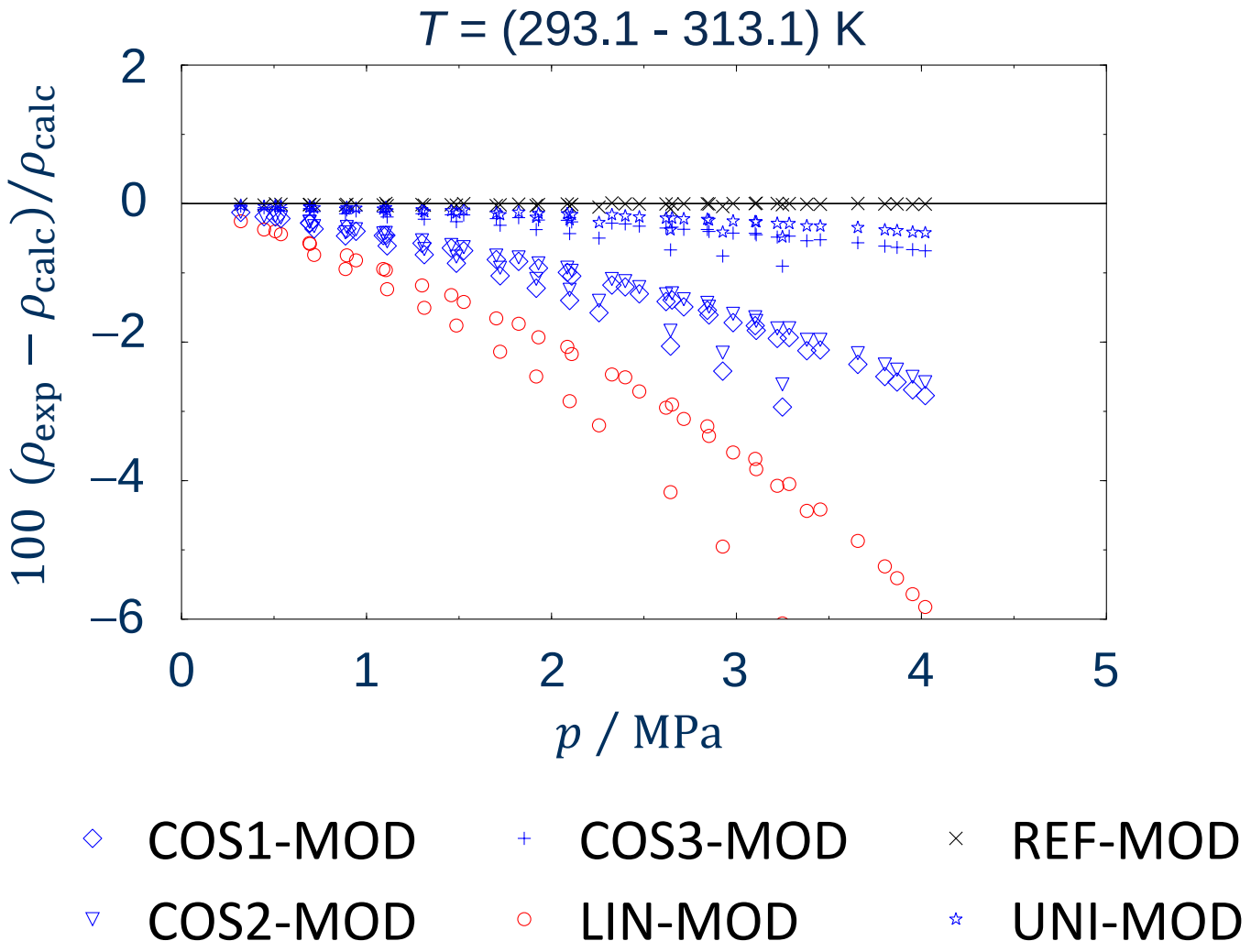

Summary

— Predictive multi-fluid mixture models and reference models have been compared to experimental data

— Investigated mixtures: CO_2+CH_4 and CO_2+C_2H_6

— Results for phase equilibria are better for UNI-MOD and COS-MOD than with LIN-MOD

— Unexpectedly, homogeneous densities are also better with UNI-MOD and COS-MOD than with LIN-MOD

— Hence, the combination of the multi-fluid mixture model with g^{E}-models seems to be better suited for screening purposed than LIN-MOD

Perspective

— Further comparisons needed:

  - Other mixtures

  - More properties (speed of sound, heat capacity, etc.)

— The effect of refitting (general) parameters of UNIFAC and COSMO-SAC should be studied

— The developed models can be used for screenings for promising mixtures

— Further development of these models: TU Dresden, suCOO-Lab

Thank you for your attention!
Questions?

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Combination of Multi-Fluid Mixture Models with g^{E}-Models

Basic idea: equate g^{E} or a^{E} at a specified reference pressure

$$g^{\mathrm{E}}_{\mathrm{EOS}}(p_0) = g^{\mathrm{E}}_{\mathrm{GE}} \qquad a^{\mathrm{E}}_{\mathrm{EOS}}(p_0) = a^{\mathrm{E}}_{\mathrm{GE}}$$

Needed: expression for a^{E} from multi-fluid mixture model

$$a^{\mathrm{E}}(T, p, \bar{x}) = a\,(T, p, \bar{x}) - RT \sum_{i=1}^{N} x_i \ln\,(x_i) - \sum_{i=1}^{N} x_i a_{\mathrm{o}i}(T, p)$$

Molar Helmholtz energy of the mixture at specified $T, p, \bar{x}$

Ideal mixing term

Molar Helmholtz energies of the pure compontents i at specified T, p

Combination of Multi-Fluid Mixture Models with g^E-Models

Molar Helmholtz energy of the **mixture** calculated with the multi-fluid mixture model

$$\frac{a(T,p,\bar{x})}{RT} = \alpha(\tau,\delta,\bar{x}) = \sum_{i=1}^{N} x_i \alpha_{\mathrm{o},i}^{\mathrm{o}}(T,\rho) + \sum_{i=1}^{N} x_i \ln(x_i) + \sum_{i=1}^{N} x_i \alpha_{\mathrm{o},i}^{\mathrm{r}}(\tau,\delta) + \alpha^{\mathrm{Dep}}(T,p,\bar{x})$$

The Helmholtz energy of the mixture needs to be evaluated at T, p und $\bar{x}$

$$\rho = \rho(T,p,\bar{x}) \rightarrow \delta = \frac{\rho(T,p,\bar{x})}{\rho_{\mathrm{red}}(\bar{x})}$$

$$\tau = \frac{T_{\mathrm{red}}(\bar{x})}{T}$$

Combination of Multi-Fluid Mixture Models with g^E-Models

Molar Helmholtz energy of the **pure components**

$$\frac{a_{\mathrm{o}i}(T,p)}{RT} = \alpha^{\mathrm{o}}_{\mathrm{o},i}(T,\rho_i) + \alpha^{\mathrm{r}}_{\mathrm{o},i}(\tau_i,\delta_i)$$

The Helmholtz energies need to be evaluated at the same T and p:

$$\rho_i = \rho_i(T,p) \;\rightarrow\; \delta_i = \frac{\rho_i(T,p)}{\rho_{\mathrm{c},i}}$$

$$\tau_i = \frac{T_{\mathrm{c},i}}{T}$$

Combination of Multi-Fluid Mixture Models with g^{E}-Models

The molar excess Helmholtz energy then becomes

$$\frac{a^{\mathrm{E}}(T,p,\bar{x})}{RT} = \sum_{i=1}^{N} x_i[\alpha^{\mathrm{o}}_{\mathrm{o},i}(T,\rho) - \alpha^{\mathrm{o}}_{\mathrm{o},i}(T,\rho_i)] + \sum_{i=1}^{N} x_i[\alpha^{\mathrm{r}}_{\mathrm{o},i}(\tau,\delta) - \alpha^{\mathrm{r}}_{\mathrm{o},i}(\tau_i,\delta_i)] + \alpha^{\mathrm{Dep}}(T,p,\bar{x})$$

With

$$\alpha^{\mathrm{o}}_{\mathrm{o},i}(T,\rho) = f_i(T) + \ln\left(\frac{\rho}{\rho_{\mathrm{c},i}}\right) \quad \text{and} \quad \alpha^{\mathrm{o}}_{\mathrm{o},i}(T,\rho_i) = f_i(T) + \ln\left(\frac{\rho_i}{\rho_{\mathrm{c},i}}\right)$$

it is

$$\frac{a^{\mathrm{E}}(T,p,\bar{x})}{RT} = \sum_{i=1}^{N} x_i \ln\left(\frac{\rho}{\rho_i}\right) + \sum_{i=1}^{N} x_i[\alpha^{\mathrm{r}}_{\mathrm{o},i}(\tau,\delta) - \alpha^{\mathrm{r}}_{\mathrm{o},i}(\tau_i,\delta_i)] + \alpha^{\mathrm{Dep}}(T,p,\bar{x})$$

Combination of Multi-Fluid Mixture Models with g^E-Models

Finally, the departure function becomes

$$\alpha^{\mathrm{Dep}}(T,p,\bar{x}) = \frac{a^{\mathrm{E}}(T,p,\bar{x})}{RT} - \sum_{i=1}^{N} x_i \ln\left(\frac{\rho}{\rho_i}\right) - \sum_{i=1}^{N} x_i [\alpha^{\mathrm{r}}_{\mathrm{o},i}(\tau,\delta) - \alpha^{\mathrm{r}}_{\mathrm{o},i}(\tau_i,\delta_i)]$$

Choice of a reference pressure:

— Like PSRK (Holderbaum and Gmehling (1991))

— Saturated liquid at $p_0 = 101325$ Pa

— Assumption of a constant packing fraction u at saturated liquid conditions

Combination of Multi-Fluid Mixture Models with g^E-Models

The following assumptions are used:

— The reference pressure is chosen as $p_0 = 101325\ \mathrm{Pa}$ (see PSRK, VTPR)

— The densities of the liquid phase at p_0 are calculated assuming (see PSRK, VTPR)

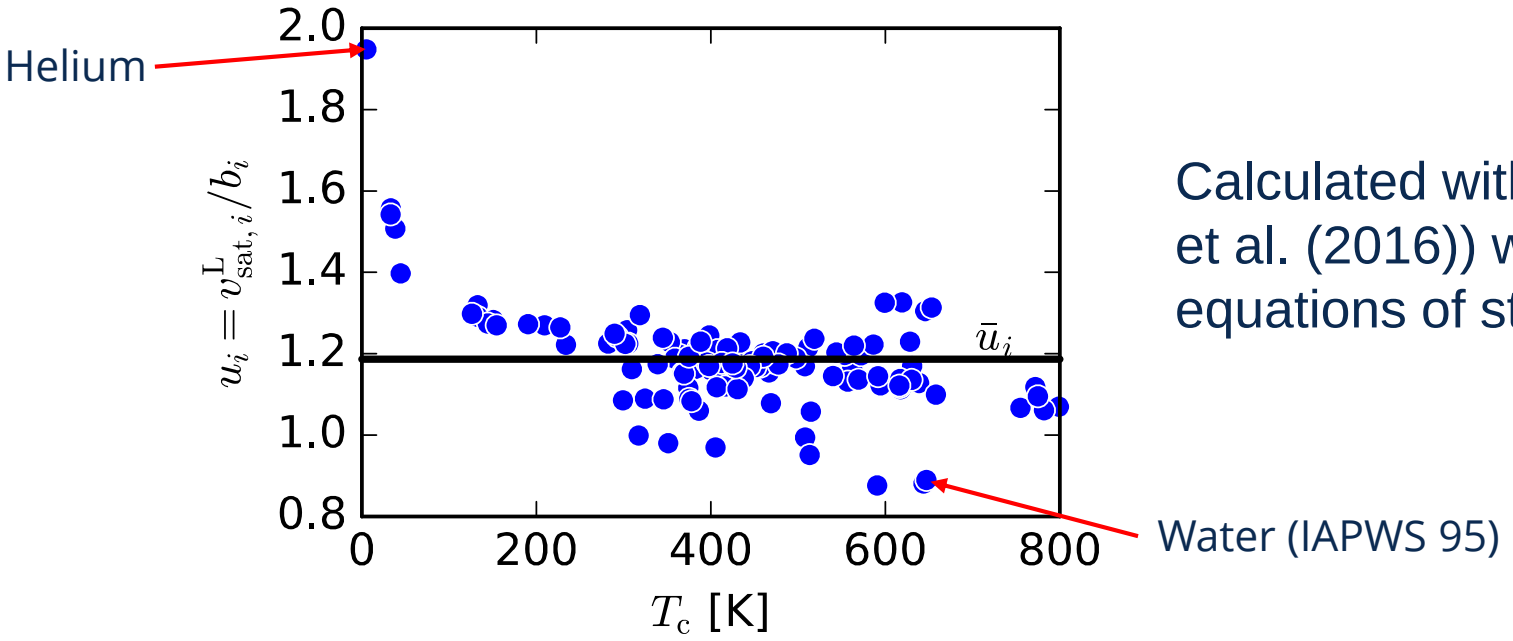
$u = 1.17 = \mathrm{const.}$ Inverse packing fraction: $u = \dfrac{v_s^{\mathrm{L}}(p_0)}{b} = \dfrac{v_{s,i}^{\mathrm{L}}(p_0)}{b_i}$

— The densities at the reference pressure then become

$$\rho_{\mathrm{ref}} = \frac{1}{ub} \quad \text{and} \quad \rho_{i,\mathrm{ref}} = \frac{1}{ub_i}$$

Combination of Multi-Fluid Mixture Models with g^E-Models

Calculated inverse packing fractions of saturated liquids at p_0



Calculated with TREND 3.0 (Span et al. (2016)) with multiparameter equations of state for 121 fluids

$\longrightarrow \quad \bar{u}_i \approx 1.17 \quad \longrightarrow$ $u = u_i = 1.17$

$\rho_{i,\mathrm{ref}} = \cancel{\frac{1}{u b_i}} \Rightarrow \rho_{i,\mathrm{ref}} = \rho_{\mathrm{s},i}(p_0)$

Combination of Multi-Fluid Mixture Models with g^E-Models

The inverse packing fraction is defined as

$$u = \frac{v^{\mathrm{L}}}{b}$$

u - Inverse packing fraction

v^{L} - Molar volume of the saturated liquid

b - covolume calculated with a cubic equation of state

For pure substances: $u_i = \frac{v_i^{\mathrm{L}}}{b_i}$ with $b_i = 0.08664 \frac{RT_{\mathrm{c},i}}{p_{\mathrm{c},i}}$

The covolume of the mixture is calculated with a linear mixing rule $b = \sum_{i=1}^{N} x_i b_i$

Combination of Multi-Fluid Mixture Models with g^E-Models

With the definition of the inverse packing fraction follows

$$\rho_{\mathrm{ref}} = \frac{1}{ub} \quad \text{and} \quad \rho_{i,\mathrm{ref}} = \frac{1}{ub_i}$$

Densities of saturated liquid at p_0

Hence, the reduced densities at reference conditions become

$$\delta_{\mathrm{ref}} = \frac{1}{ub\rho_{\mathrm{r}}} \quad \text{and} \quad \delta_{i,\mathrm{ref}} = \frac{1}{ub_i\rho_{\mathrm{c},i}}$$

And therefore the departure function

$$\alpha^{\mathrm{Dep}} = \frac{a^{\mathrm{E}}}{RT} - \sum_{i=1}^{N} x_i \ln\left(\frac{b_i}{b}\right) - \sum_{i=1}^{N} x_i\left[\alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta_{\mathrm{ref}},\tau) - \alpha_{\mathrm{o}i}^{\mathrm{r}}\left(\delta_{i,\mathrm{ref}},\tau_i\right)\right]$$

Combination of Multi-Fluid Mixture Models with g^E-Models

The residual part should hold: $\lim_{\rho \to 0} \alpha^r = 0$. Therefore, a density dependent term is needed.

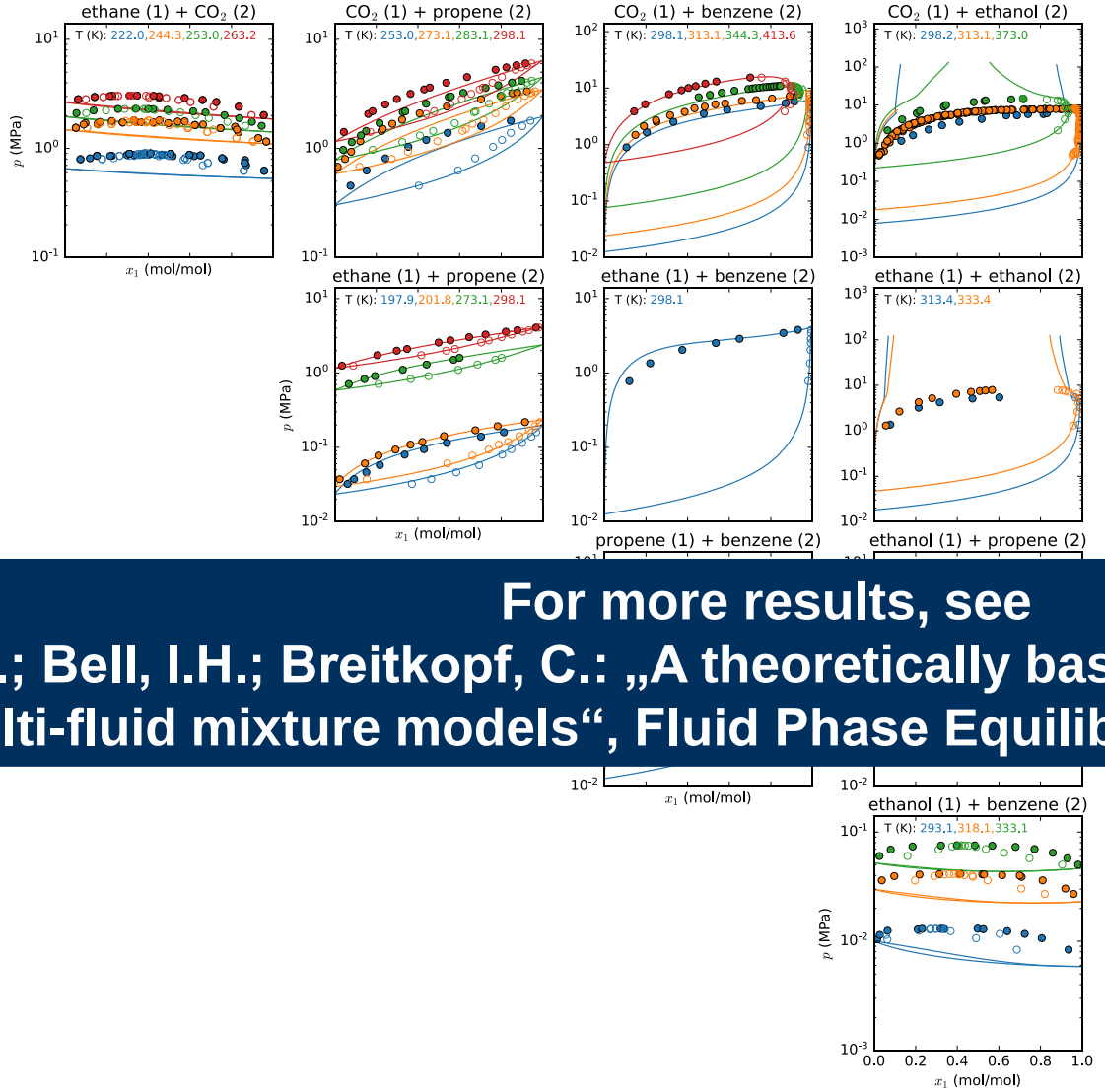
Translating the PSRK to the reduced residual Helmholtz energy, the following is obtained

$$\alpha^r_{PSRK} = -\ln(1-b\rho) + \frac{\ln(1+b\rho)}{\ln\left(1+\frac{1}{u}\right)}\left\{\frac{g^E_{GE}}{RT} - \sum_{i=1}^{N} x_i \ln\left(\frac{b_i}{b}\right) - \frac{1}{RT}\ln\left(1+\frac{1}{u}\right)\sum_{i=1}^{N} x_i \frac{a_i}{b_i}\right\}$$

Applying the density dependent term of the PSRK yields:

$$\alpha^{Dep} = \frac{\ln(1+b\rho)}{\ln\left(1+\frac{1}{u}\right)}\left\{\frac{a^E_{GE}}{RT} - \sum_{i=1}^{N} x_i \ln\left(\frac{b_i}{b}\right) - \sum_{i=1}^{N} x_i \left[\alpha^r_{oi}(\delta_{ref}, \tau) - \alpha^r_{oi}(\delta_{i,ref}, \tau_i)\right]\right\}$$

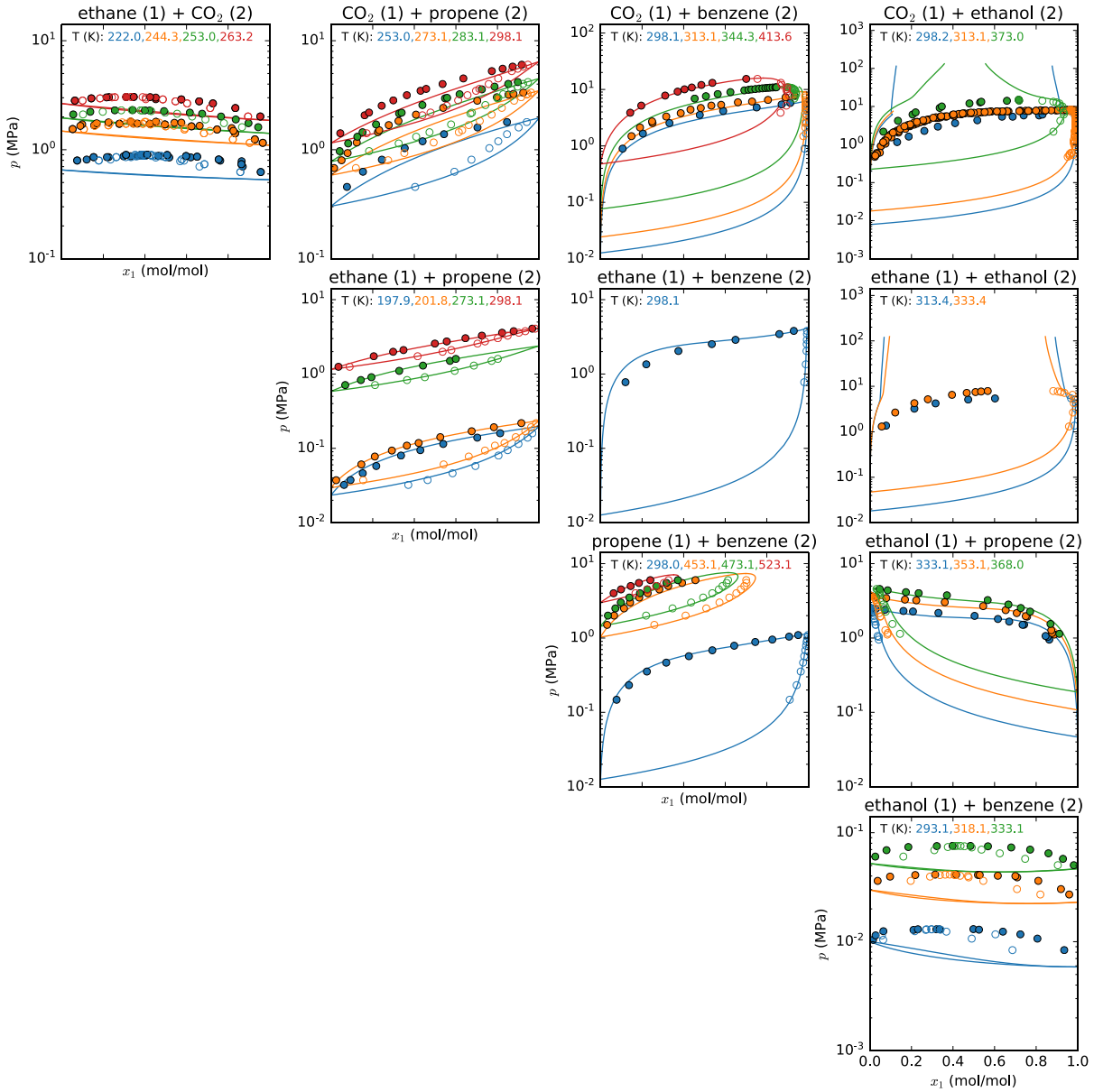
Results for All Binary Mixtures With Linear Mixing Rules



For more results, see
Jäger, A.; Bell, I.H.; Breitkopf, C.: „A theoretically based departure function for multi-fluid mixture models“, Fluid Phase Equilibria 469, 56-69, 2018.

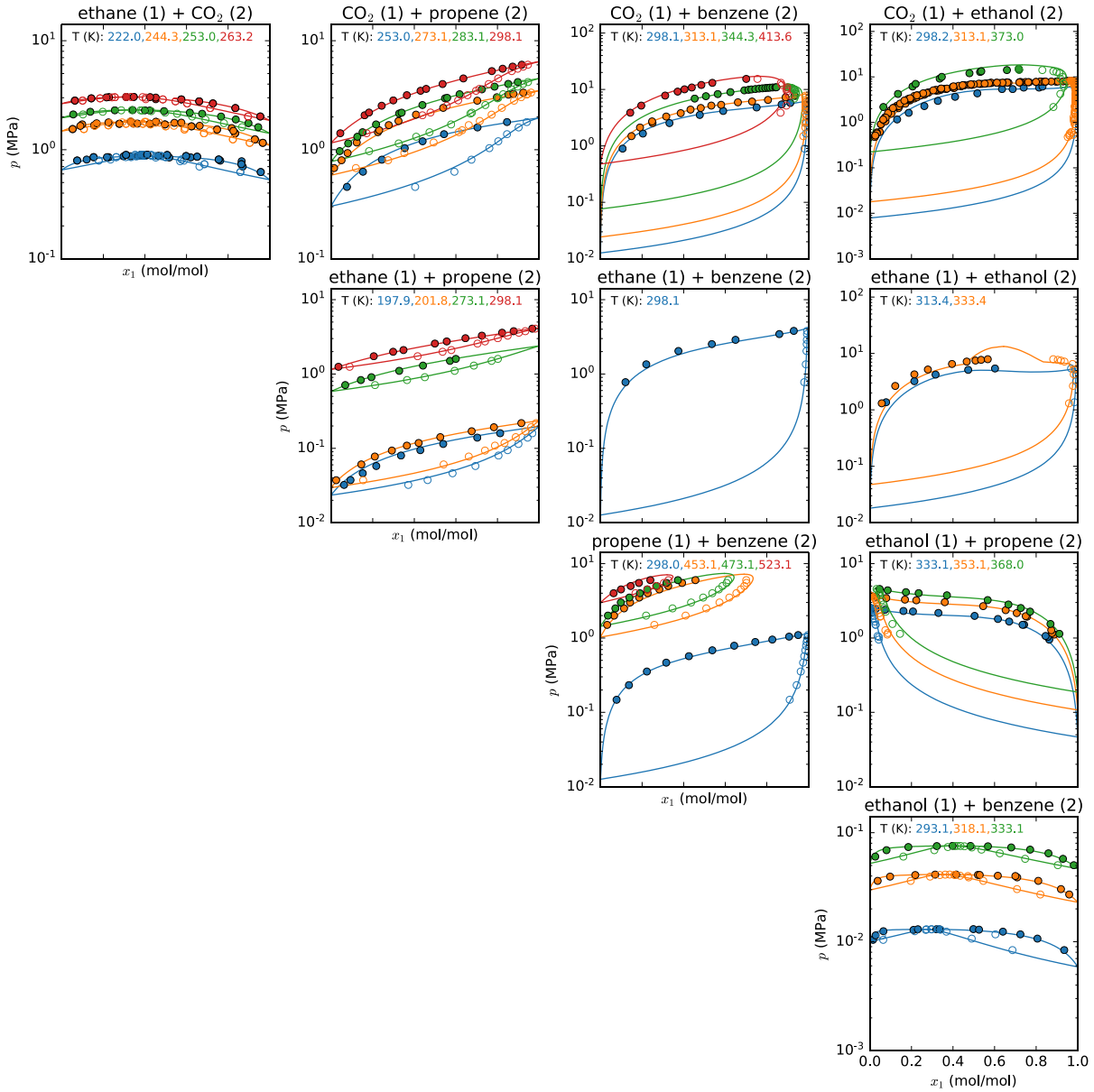
Results for all binary mixtures

— Linear mixing rules



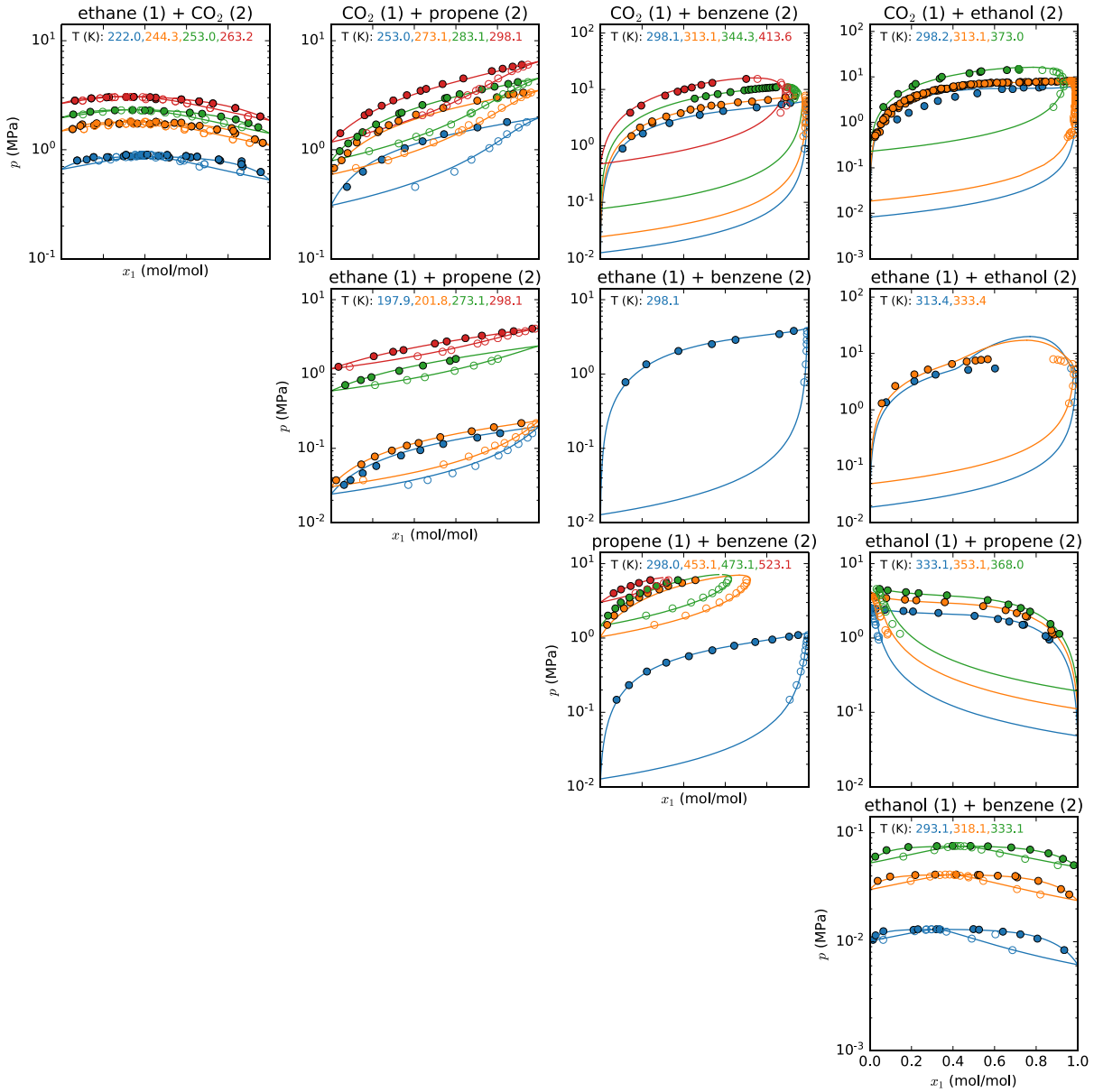
Results for all binary mixtures

— New model with fitted parameters



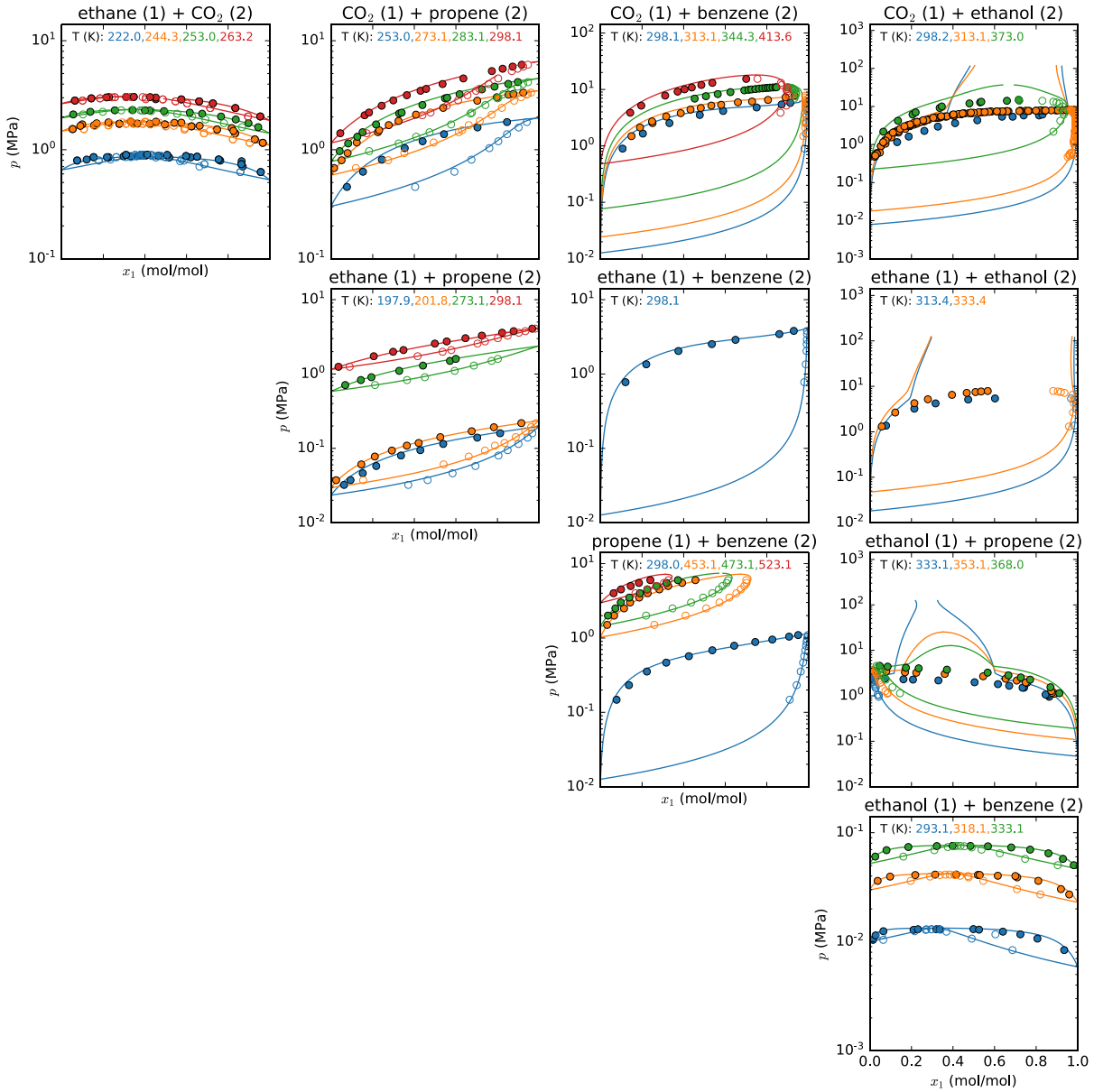
Results for all binary mixtures

— New model with PSRK parameters



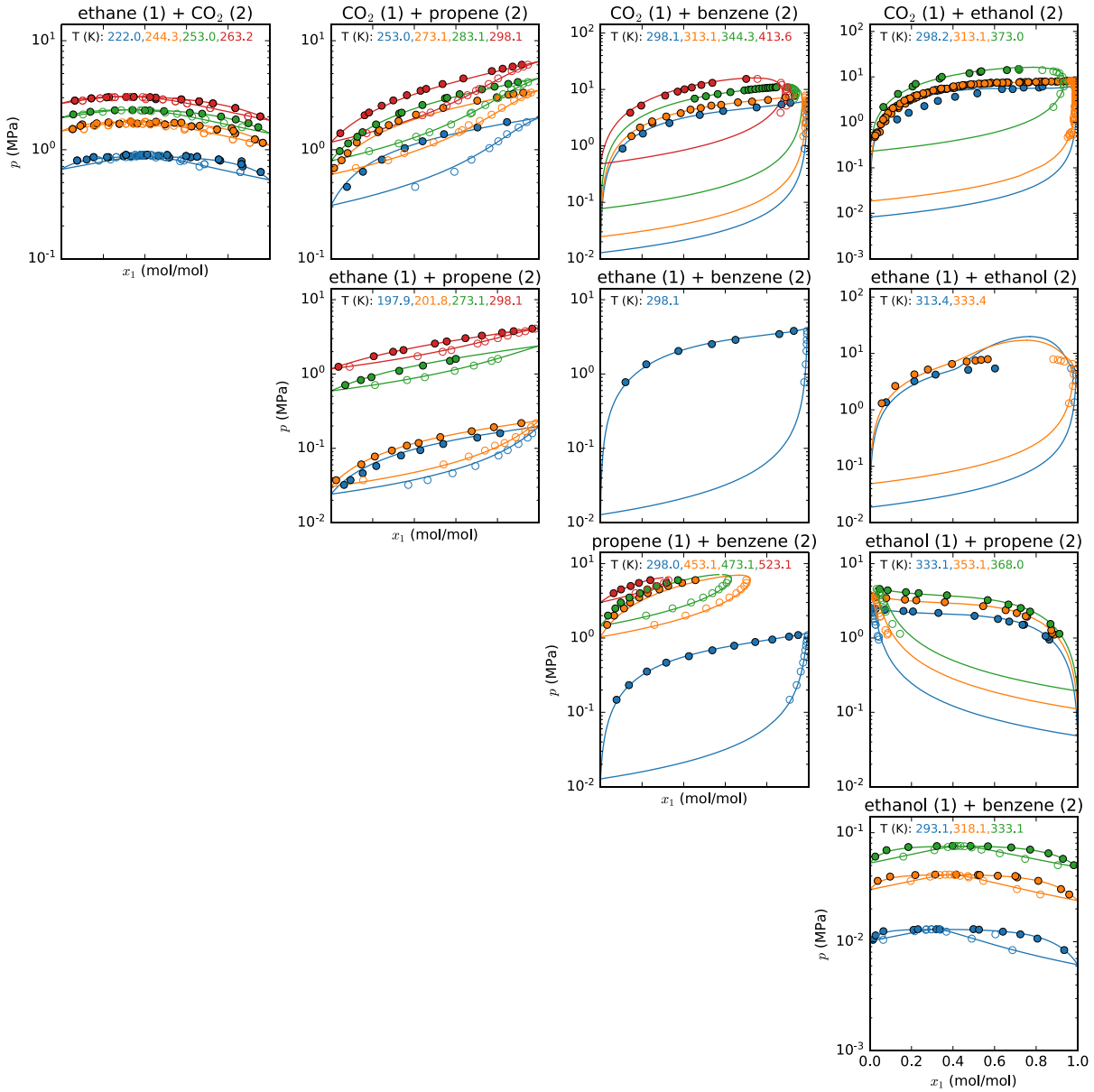
Results for all binary mixtures

— New model with VTPR parameters



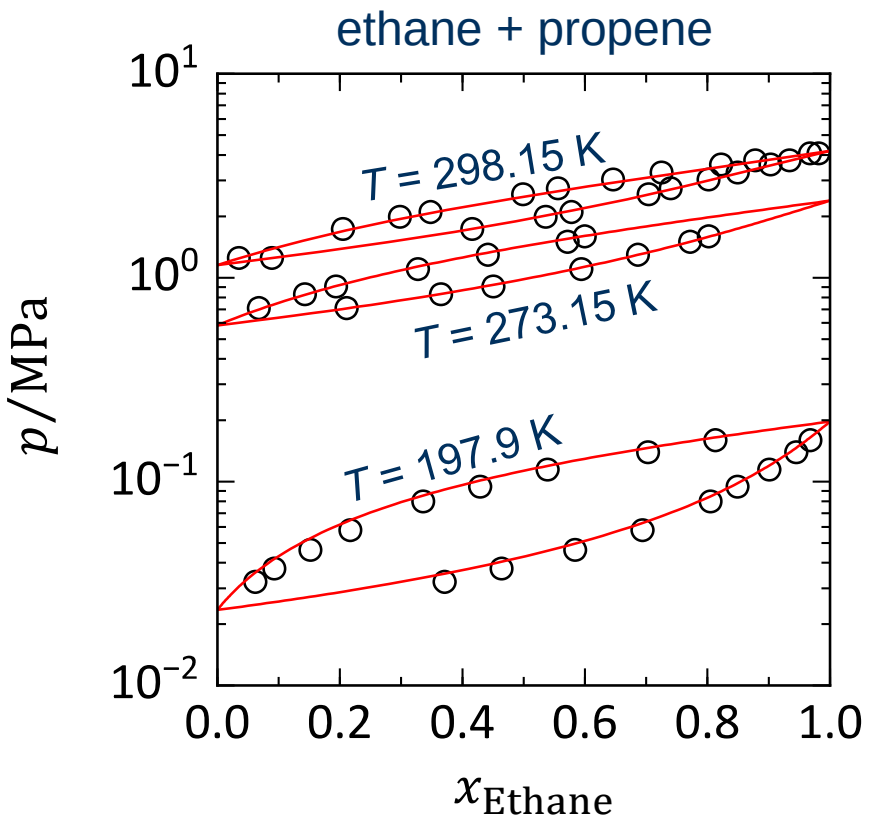
Results for all binary mixtures

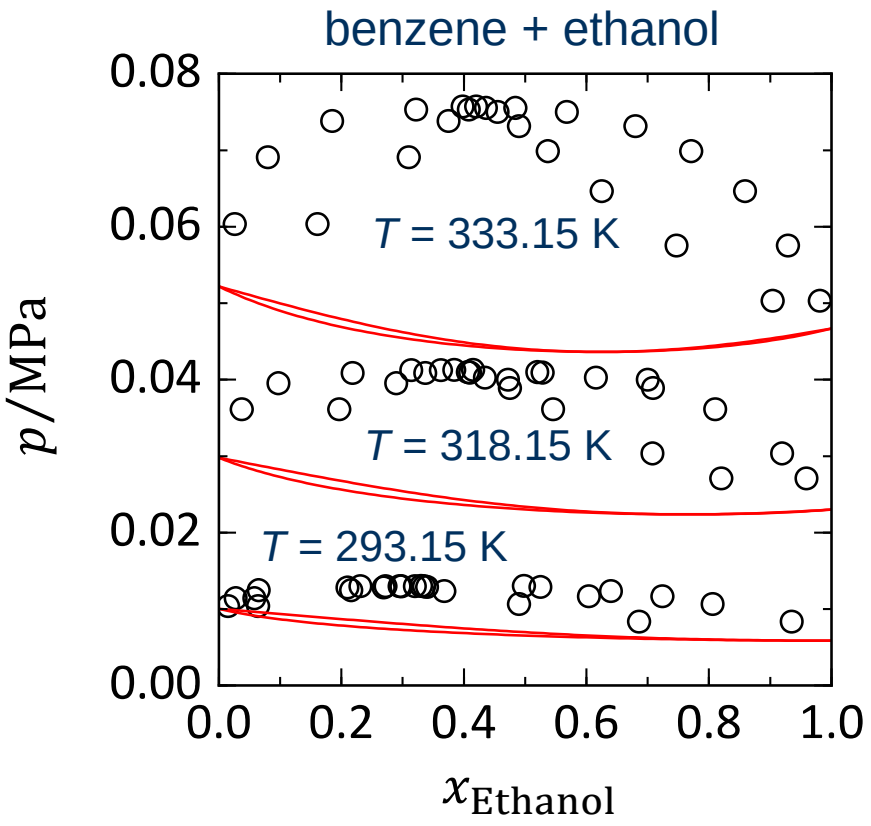
— Results of full PSRK



Results with Standard Mixing Rules

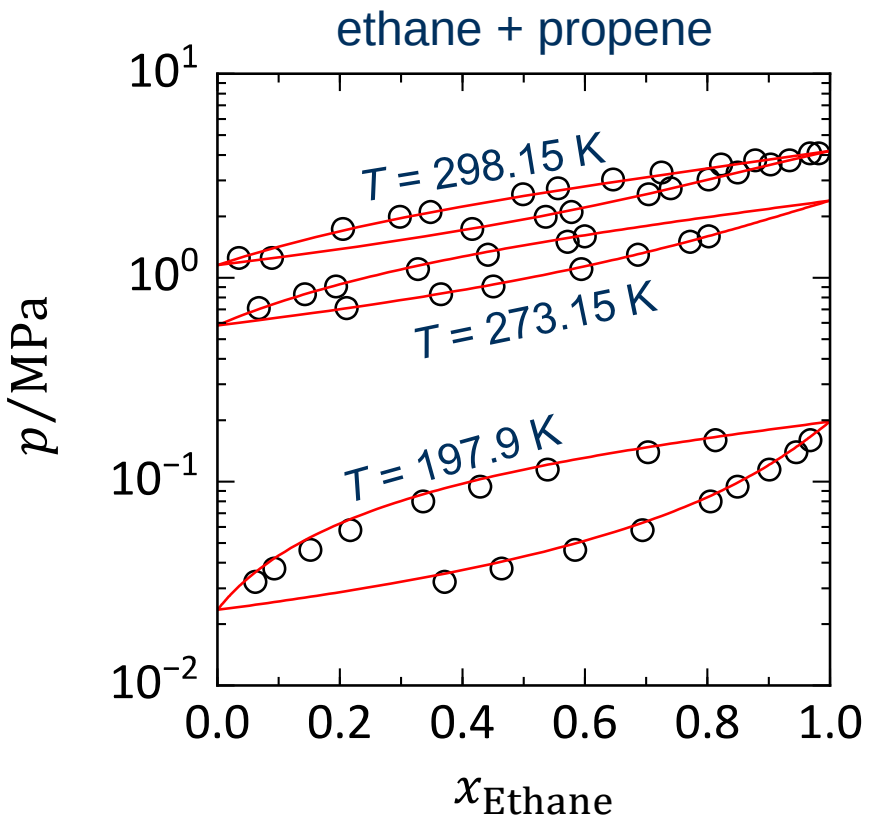
Results for ethane + propene and benzene + ethanol with **linear mixing rules**

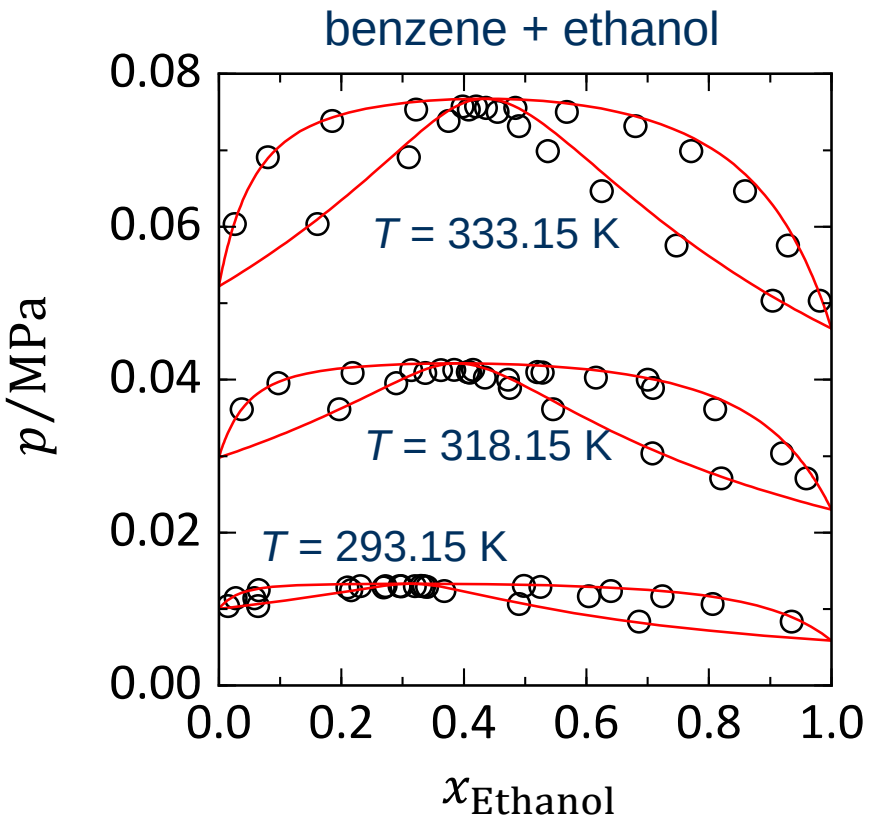




Results of the New Model with UNIFAC (VTPR) Parameters

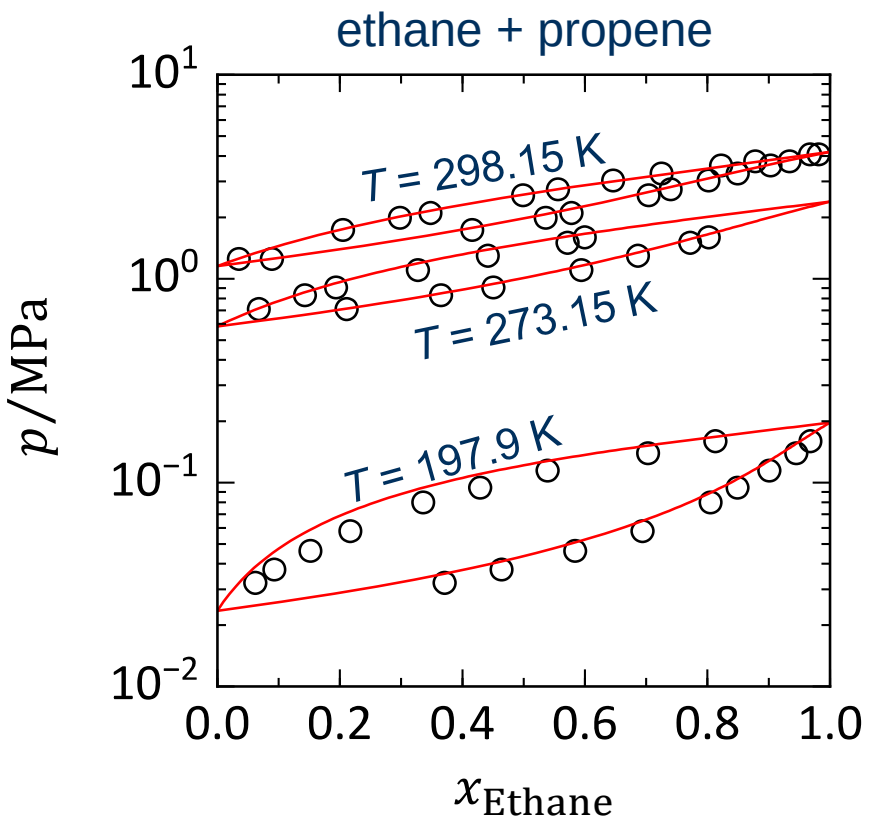
Results for ethane + propene and benzene + ethanol with VTPR parameters for UNIFAC

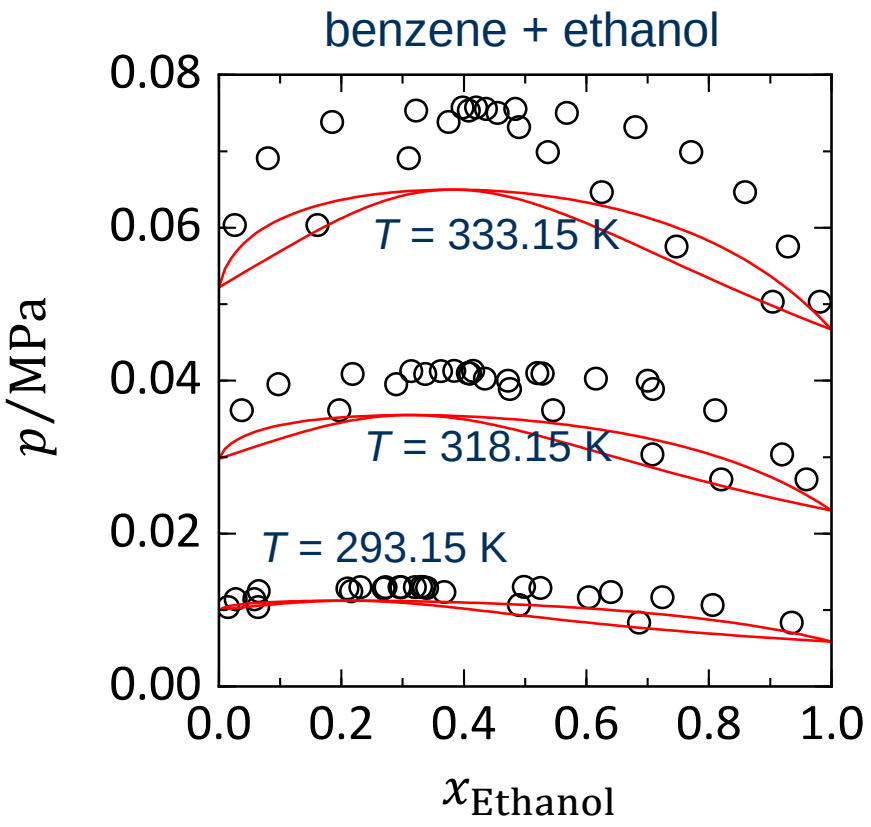




Results of the new model with COSMO-SAC (Mullins et al. 2006)

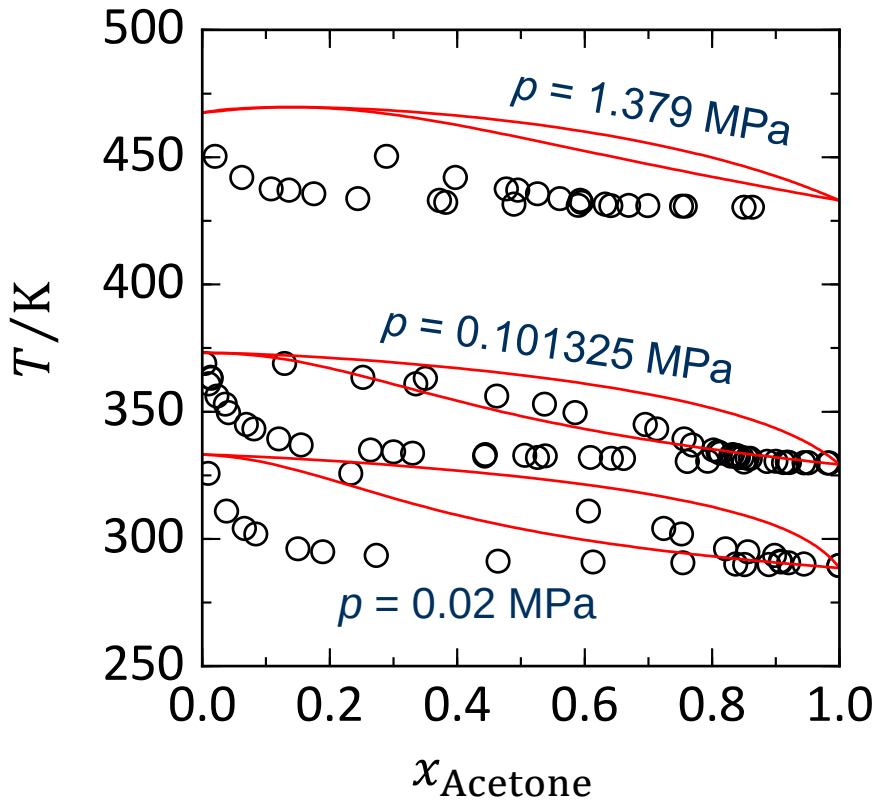
Results for ethane + propene und benzene + ethanol with COSMO-SAC





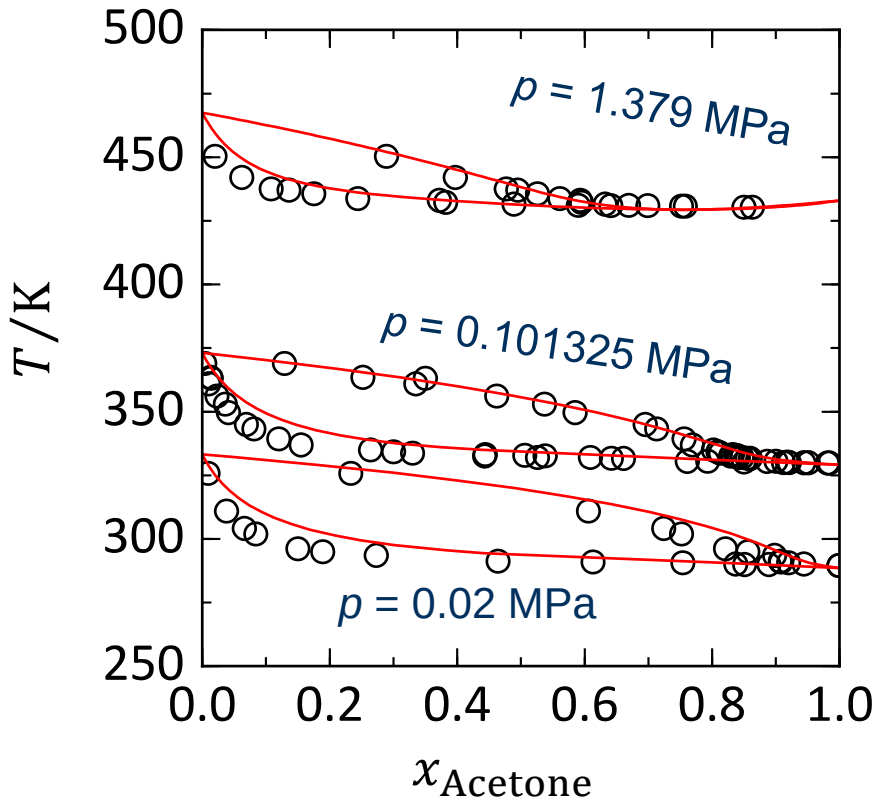
Results for mixtures with water: water + acetone

Results for acetone + water with **linear mixing rules**



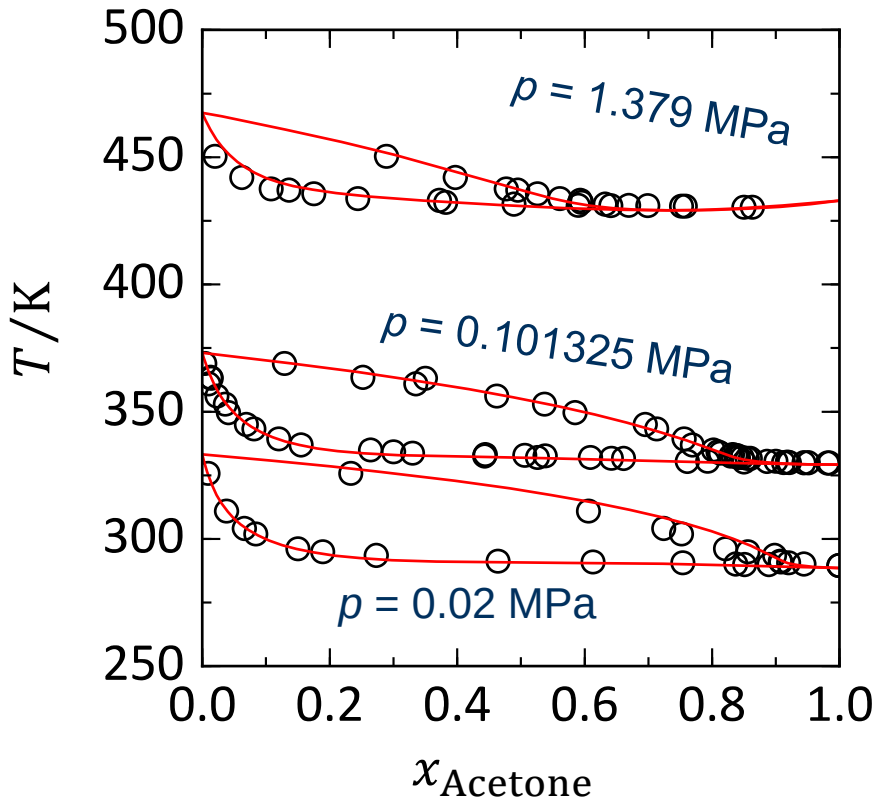
Results for mixtures with water: water + acetone

Results for acetone + water with **VTPR parameters for UNIFAC**



Results for mixtures with water: water + acetone

Results for acetone + water with partly **fitted VTPR parameters for UNIFAC**



Fitted to data:

$a_{79}, b_{79}, c_{79}, a_{97}, b_{97}, c_{97}$